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<b>(51) International Patent Classification <sup>3</sup>:</b>  C08L 63/04	<b>A1</b>	<b>(11) International Publication Number:</b> WO 81/01857  <b>(43) International Publication Date:</b> 9 July 1981 (09.07.81)
<p><b>(21) International Application Number:</b> PCT/US80/01702</p> <p><b>(22) International Filing Date:</b> 18 December 1980 (18.12.80)</p> <p><b>(31) Priority Application Number:</b> 107,019</p> <p><b>(32) Priority Date:</b> 26 December 1979 (26.12.79)</p> <p><b>(33) Priority Country:</b> US</p> <p><b>(71) Applicant:</b> THE POLYMER CORPORATION [US/US]; 2120 Fairmont Avenue, Reading, PA 19605 (US).</p> <p><b>(72) Inventor:</b> GRAY, Kenneth, W.; 512 High Boulevard, Mifflin Park, PA 19607 (US).</p> <p><b>(74) Agent:</b> CHURCH, Richard, O.; The Polymer Corporation, P.O. Box 422, Reading, PA 19603 (US).</p>		<p><b>(81) Designated States:</b> AT (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), JP, LU (European patent), NL (European patent), SE (European patent).</p> <p><b>Published</b> <i>With international search report</i></p>
<p><b>(54) Title:</b> CHEMICAL RESISTANT COATINGS</p> <p><b>(57) Abstract</b></p> <p>The stain and chemical resistance of coatings applied by fusion coating process is increased by melt blending a minor amount of a hydrophobic silica aerogel into the coating powders.</p>		

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Chemical Resistant CoatingsTechnical Field

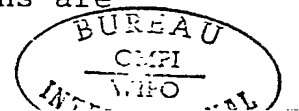
This invention relates to coating powders and more particularly to coating powders that are especially adapted to yield coatings that are resistant to staining  
5 and chemical degradation.

Background Art

The coating compositions of this invention are dry, free-flowing powders adapted for application to substrates by fusion coating processes. The term "fusion coating  
10 processes" is here used to mean those coating processes in which powders are distributed over a substrate and heated to above their melting points to fuse them into a continuous protective film. The powders may be based either on thermoplastic resins or thermosetting resins  
15 and, in the latter case, the heating must be sufficient to cure the resins and develop their ultimate properties. Examples of fusion coating processes include fluidized bed, electrostatic spraying, hot flocking, cloud chambers, fluid transport of powder through heated pipe, and the  
20 like.

The environment in which coated articles are used may require that their coatings be resistant to staining and corrosion for either decorative or functional reasons. For example, decorative coatings are applied to kitchen  
15 appliances which lose their attractiveness when they became stained by such things as fruit and vegetable juices, catsup, mustard, or the like. At the other extreme are functional coatings which may be used in the oil fields to protect pipe and tubing from the corrosive effects of such things as brine, drilling muds and acid  
30 forming gases at pressures as high as 700 kg/cm<sup>2</sup> and temperatures which not uncommonly reach 200°C.

In the past, it has been conventional to formulate highly resistant coatings from phenolic and epoxy/phenolic  
35 resins and apply them from solutions. These resins are



difficult to use in fusion coating processes because they cure, at least in part, by condensation reactions which generate water and gases that form voids in the protective films unless they are cured under pressure  
5 or are applied in comparatively thin layers.

#### Disclosure of the Invention

Accordingly, it is an object of this invention to provide coatings that are stain and corrosion resistant.

Another object of this invention is to provide  
10 coating powders that will provide dense, void free, highly chemical and temperature resistant films when applied by fusion coating methods.

These and other objects of this invention are achieved by melt mixing a small amount of an extremely  
15 hydrophobic material with coating powders. At concentrations even as low as .5%, significant improvement in stain and corrosion resistance has been observed. The preferred hydrophobic materials for use in this invention are fumed silicas which have been treated by  
20 reacting the surface silanol groups with a silane to tie up the free hydroxyl groups and provide a hydrophobic surface.

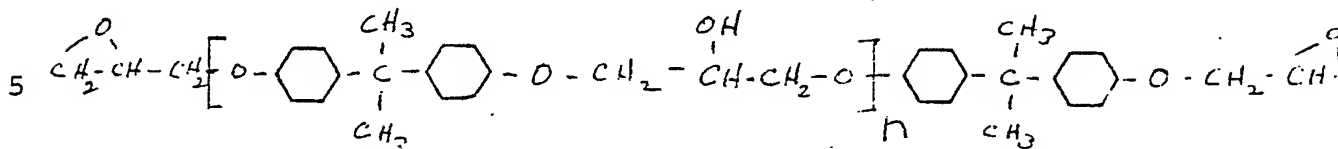
A suitable hydrophobic silica for use in this invention is sold by Tulco, Inc. under its trademark  
25 Tullanox 500. This material is described as a fumed silica having a nominal particle size of 0.007 microns and a theoretical surface area of 325 square meters per gram. The surface of the fumed silica is chemically treated to replace the silanol groups with trimethyl-  
30 siloxyl groups.

Another similar hydrophobic material is manufactured by Degussa under its trademark Aerosil R 972. This material is described as having particle sizes in the range of from .005 to .050 microns, surface areas of from  
35 50 to 400 square meters per gram, and surfaces that have been made hydrophobic by reacting the silanol groups on the silica surface with alkyl chlorosilane.



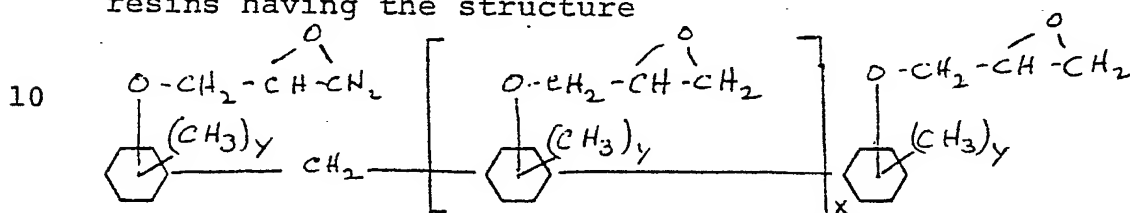
In the following examples:

DGEBA refers to diglycidal ethers of bisphenol A epoxy resins having the structure:



and the numerical designation of the type approximates the value of n;

Epoxy novolac resins refers to epoxidized novolac resins having the structure



in which the epoxy functionality is approximately  $x + 2$  and y may be 0 or 1; and

phr is used to mean parts by weight per hundred parts by weight of resin.

#### 15 EXAMPLE I

The following components were blended together:

	phr
DGEBA - type 7 epoxy resin	36.0
DGEBA - type 4 epoxy resin	36.0
DGEBA - type 3 epoxy resin	15.2
20 Epoxy-novolac (epoxy functionality 3.2)	12.8
Polyalkylacrylate flow promoter	0.8
Dicyandiamide	4.36
2-methylimidazole	0.2
Silica filler	100.0
25 TiO <sub>2</sub>	10.0
Cr <sub>2</sub> O <sub>3</sub> (green pigment)	20.0
Surfactant (Dow Corning DC 2106)	0.67
Hydrophobic silica (Silanox 101)	1.0

30 The above materials were melt-mixed in an extruder and the extrudate was chopped and ground to a fine powder that all passed through a 60 mesh screen. 0.67 phr of an untreated hydrophilic silica aerogel was dry blended

to promote powder flow. Test panels prepared for coating by sand blasting, deburring cleaning, degreasing and priming were heated to a temperature of 165°C. The panels were coated by immersing them in a fluidized bed of the powders and postheated for 30 minutes at 205°C. to complete the curing of the coatings.

A uniform film thickness of from about 10 to 15 mils was obtained and when the coatings were evaluated in qualification testing for use as coatings for water flood pipe, they were found to be superior to the industry standards including liquid and solid epoxy systems and liquid epoxy/phenolics.

#### EXAMPLE II

A coating powder was compounded as in Example I by melt-mixing the following ingredients:

	<u>phr</u>
DGEBA - type 4 epoxy resin	50
Epoxy novolac - functionality 3.8	50
Diamino diphenyl sulfone (curing agent)	20
20 CaSiO <sub>3</sub> (Nycore 300)	125
TiO <sub>2</sub> (R-900)	10.0
Pigment (Green Cr <sub>2</sub> O <sub>3</sub> )	20.0
BCl <sub>3</sub> -amine complex (catalyst)	1.0

The blended materials were chopped and ground to form a powder that passed through a 60 mesh screen and 0.67 phr of an untreated hydrophilic fumed silica was dry blended to improve powder flow.

#### EXAMPLE III

A coating powder identical to that of Example II was prepared in which 1.0 phr of the hydrophobic silica of this invention (Tullanox 500) was included in the melt mixed materials.

Panels were sand blasted, deburred, cleaned, degreased and primed and then coated with the powders of Examples II and III. The coatings were applied by pre-heating the panels to 190°C., immersing them in a fluidized bed of the coating powders, and then postheating them for 60 minutes at 220°C. Smooth, uniform coatings of



approximately 10 mils were obtained.

The coated panels were immersed to 2/3 of their length in a given test solution and the solution was then purged with hydrogen sulfide. After the autoclave was sealed, it was charged with 140 psi of CO<sub>2</sub> and the pressure was increased to 2,800 psi with air. The temperature was raised to 150°C. and these conditions were maintained for 24 hours. The test solutions used were four drilling muds including weighted lignosulfate, Baroid K Plus (TM N.L. Baroid), salt water polymer and fresh water polymer. In all of the tests, the coatings of Example IV which included the hydrophobic silica proved significantly superior in resistance to attack by the drilling muds and dissolved gases than did the coatings of Example II.

#### EXAMPLE IV

	<u>phr</u>
DGEBA - type 3 epoxy resin	8.0
DGEBA - type 4 epoxy resin	17.0
20 Epoxy-novolac (epoxy functionality 3.2)	3.0
Polyalkylacrylate flow promoter	0.8
Dicyandiamide	4.36
2-methylimidazole	0.2
Silica filler	100.0
25 TiO <sub>2</sub>	10.0
Cr <sub>2</sub> O <sub>3</sub> (green pigment)	20.0
Surfactant (Dow Corning DC 2106)	0.67
Hydrophobic silica (Silanox 101)	2.0

The above materials were melt-mixed in an extruder and the extrudate was chopped and ground to a fine powder that all passed through a 60 mesh screen. 0.67 phr of an untreated hydrophilic silica aerogel was dry blended to promote powder flow.

Steel panels were degreased, cleaned and primed. The panels were preheated for 5 minutes to a temperature of 205°C. and then immersed in the fluidized bed until a 10-15 mil coating had adhered to the steel panel. The panel was placed in an oven and postheated for 30 minutes



at 190°C.

EXAMPLE V

5 A coating material was prepared that was identical to that of Example I except that 0.5% of a hydrophobic fumed silica (Tullanox 500) was included in the formulation. A steel panel was coated with this powder in a similar manner to the panel in Example IV.

10 The steel panels coated in Example IV and Example V were compared by exposing them to common foods that readily cause staining such as grape juice, red beet juice, catsup and mustard. It was found that the panels coated with the composition of Example IV was permanently stained when exposed to these foods whereas the panels coated with a composition of Example V resisted staining and  
15 the foods were easily wiped away leaving no trace of color.

\* \* \* \*

In the above examples a significant improvement in chemical resistance was obtained using as little as 0.5  
20 phr of the hydrophobic silica. Larger quantities can be used but, as a practical matter, when the amount of silica approaches 3 phr, its thixotropic effect makes it impossible to obtain adequate melt flow of the coating powders.

25 A related advantage that accrues in the practice of this invention is that the hydrophobic silicas are also extremely oleophilic. Oil will adhere to substrates coated with these materials which will provide lubricity and reduce wear in those applications in which the  
30 substrate is used in moving contact with other surfaces. It is also believed that an oil film over a coated surface will be further protection from attack by water borne chemical agents.

In the preferred form of this invention, the hydrophobic silica aerogels are used in coating powders based  
35 upon epoxy resins having epoxy functionalities of greater than 2, as can be achieved through the use of epoxy novolacs. Also, high filler loadings of at least 50





parts per hundred parts resin are believed to contribute the chemical resistance of the coatings.



Claims

1. A powdered coating composition adapted for application in fusion coating processes to provide a coating having a high degree of resistance to staining and chemical attack, the improvement comprising melt  
5 mixing minor amounts of a hydrophobic fumed silica into the coating powders.

2. A coating powder according to Claim 1 wherein the hydrophobic fumed silica is used in amounts from 0.5 to about 3 parts per hundred parts of resin and  
10 has a particle size less than 0.05 microns and a surface area in excess of 50 square meters per gram.

3. A coating powder according to Claim 2 wherein the resin is an epoxy.

4. A coating composition according to Claim 3  
15 wherein the epoxy resin includes an epoxy novolac resin.

5. A coating powder according to Claim 4 wherein the epoxy novolac has a functionality greater than 3.

6. A coating powder according to Claim 5 wherein the epoxy novolac is present in an amount in excess of  
20 25 parts per hundred parts resin.

7. A method of improving the stain and chemical resistance of coating powders which comprises melt mixing between 0.5 and 5.0 parts per hundred parts resin of a hydrophobic fumed silica into an epoxy based resin.

25 8. A method according to Claim 7 wherein the epoxy resin includes a major portion of an epoxy novolac having an epoxy functionality greater than 3.



# INTERNATIONAL SEARCH REPORT

International Application No PCT/US80/01702

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL. <b>3 C08L 63/04</b> US CL. <b>260/37EP</b>																										
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched <sup>4</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="padding: 5px; vertical-align: top;">US</td> <td style="padding: 5px; vertical-align: top;">260/37EP, 42.15</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup></div>			Classification System	Classification Symbols	US	260/37EP, 42.15																				
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>14</sup></b> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category *</th> <th style="border-bottom: 1px solid black;">Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup></th> <th style="width: 15%; border-bottom: 1px solid black;">Relevant to Claim No. <sup>18</sup></th> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">US, A, 3,661,810, PUBLISHED 09 MAY 1972, GAHMIG</td> <td style="text-align: center; vertical-align: top;">1 &amp; 2</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">US, A, 3,909,487, PUBLISHED 30 SEPTEMBER 1975, WAGGONER</td> <td style="text-align: center; vertical-align: top;">1 &amp; 2</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">US, A, 3,338,863, PUBLISHED 29 AUGUST 1967, HAAG</td> <td style="text-align: center; vertical-align: top;">1-8</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;">US, A, 3,939,087, PUBLISHED 17 FEBRUARY 1976, VIJAYENDRAN ET AL</td> <td style="text-align: center; vertical-align: top;">1-8</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;">US, A, 3,907,734, PUBLISHED 23 SEPTEMBER 1975, TEN BROECK ET AL</td> <td style="text-align: center; vertical-align: top;">1-8</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;">US, A, 4,169,187, PUBLISHED 25 SEPTEMBER 1979, GLAZAR</td> <td style="text-align: center; vertical-align: top;">1-8</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td style="vertical-align: top;">US, A, 3,396,140, PUBLISHED 06 AUGUST 1968, WELLER</td> <td style="text-align: center; vertical-align: top;">1-8</td> </tr> </table>			Category *	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>	X	US, A, 3,661,810, PUBLISHED 09 MAY 1972, GAHMIG	1 & 2	X	US, A, 3,909,487, PUBLISHED 30 SEPTEMBER 1975, WAGGONER	1 & 2	X	US, A, 3,338,863, PUBLISHED 29 AUGUST 1967, HAAG	1-8	A	US, A, 3,939,087, PUBLISHED 17 FEBRUARY 1976, VIJAYENDRAN ET AL	1-8	A	US, A, 3,907,734, PUBLISHED 23 SEPTEMBER 1975, TEN BROECK ET AL	1-8	A	US, A, 4,169,187, PUBLISHED 25 SEPTEMBER 1979, GLAZAR	1-8	A	US, A, 3,396,140, PUBLISHED 06 AUGUST 1968, WELLER	1-8
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: <sup>16</sup></p> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> </div> <div style="width: 45%;"> <p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p> </div> </div>																										
<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; vertical-align: bottom;">           Date of the Actual Completion of the International Search <sup>2</sup>   <b>12 FEBRUARY 1981</b> </td> <td style="width: 50%; border-bottom: 1px solid black; vertical-align: bottom;">           Date of Mailing of this International Search Report <sup>3</sup>   <div style="text-align: center; font-size: 1.2em; font-weight: bold;">26 FEB 1981</div> </td> </tr> <tr> <td style="border-bottom: 1px solid black; vertical-align: bottom;">           International Searching Authority <sup>1</sup>   <b>ISA/US</b> </td> <td style="border-bottom: 1px solid black; vertical-align: bottom;">           Signature of Authorized Officer <sup>19</sup>  <div style="text-align: center;"> <b>L. T. JACOBS</b> </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <sup>2</sup>  <b>12 FEBRUARY 1981</b>	Date of Mailing of this International Search Report <sup>3</sup>  <div style="text-align: center; font-size: 1.2em; font-weight: bold;">26 FEB 1981</div>	International Searching Authority <sup>1</sup>  <b>ISA/US</b>	Signature of Authorized Officer <sup>19</sup> <div style="text-align: center;"> <b>L. T. JACOBS</b> </div>																				
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**FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET**

A

US, A, 3,242,131, PUBLISHED 22 MARCH 1966,  
PEERMAN

1-8

**V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE <sup>10</sup>**

**This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:**

1. ☐ Claim numbers \_\_\_\_\_ because they relate to subject matter<sup>1,2</sup> not required to be searched by this Authority, namely:

2. ☐ Claim numbers \_\_\_\_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING <sup>11</sup>

**This International Searching Authority found multiple inventions in this international application as follows:**

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims: it is covered by claim numbers:

**Remark on Protest**

- ☐ The additional search fees were accompanied by applicant's protest.